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(54) **Electro depositing resin coatings**

(57) The formation of a clear even film of an anaphoretic resin upon the surface of a metallic substrate has been discovered to be attainable provided that the surface to be coated is formed from nickel, stainless steel or aluminium (or anodised aluminium) and a suitable resin is deposited under carefully controlled conditions. This is especially advantageous in that the film can be dyed to produce an even colouring. The preferred resins are acrylic resins, polyester resin, modified alkyd resins or combinations thereof.

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SPECIFICATION

Resin deposition

This invention relates to processes for the deposition of a dyeable resin coating upon metallic substrates which may incorporate a dyeing procedure and to the products of those processes.

The application of clear protective resin coatings to electrodeposited or polished metal surfaces in order to protect them against corrosion is well known. The process is commonly termed lacquering although it is used to include coatings which are cured by polymerisation or cross-linking as well as coatings which cure only by loss of solvent. Initially such coatings were applied by spraying or dipping the substrate but these procedures are disadvantageous in that it is difficult to obtain an even coating of the resin on the substrate. Uneven coating leads to areas of low corrosion resistance and also renders dyeing processes to colour the resin coating less attractive in that a correspondingly uneven colouring is obtained.

More recently the introduction of electrodepositable resins has meant that even coatings of resin could be applied. However attempts to produce a clear coating of an anodic resin on a metallic substrate have not been successful in that coloured or imperfect coatings were formed. As a result clear anodic electrodepositable lacquers have not been used to coat highly polished or electroplated surfaces where visual appeal is important but only as primer coatings or coloured resins where colouring is unimportant or as pigmented coatings.

We have now discovered that the difficulties in obtaining a fault free clear coating of anodic resin appear to be associated with the nature of the surface of the substrate in that clear coatings can be deposited onto surfaces which are formed from nickel, stainless steel or aluminium. Clear coatings cannot be formed on other surfaces e.g. copper, brass, silver, zinc or steel. Accordingly from one aspect our invention provides a process for the production of a film of an anodic resin on the surface of a substrate by electrodeposition which is characterised in that the surface is formed from nickel, stainless steel or aluminium and the resin is a clear resin.

The process is effective in depositing a clear resin coating onto any substrate having a surface layer of nickel, stainless steel or aluminium (or anodised aluminium). The surface layer is preferably at least 2 microns and more preferably at least 4 microns thick. Thus any substrate can be coated with resin if for example it is first plated with a surface layer of nickel prior to the deposition of the resin. Surfaces formed from other metals e.g. steel leads to the formation of discoloured coatings and thus the whole surface of the substrate is preferably formed from nickel, stainless steel or aluminium.

The suitability of any anaphoretic resin for use in the processes according to this invention must be determined empirically. Any anaphoretic resin is potentially suitable and may be selected for trial. Examples of resins which are anaphoretic include acrylic resins, polyester resins, epoxy resins and modified alkyd resins (which resins may be used in combination). The preferred resins for present use are of the acrylic or acrylic/modified polyester type. The criteria for assessing the suitability of these resins is simply that they should be capable of being deposited upon the substrate to give a clear even coating of resin which is free from pitting and other imperfections and provides the desired mechanical properties after curing. The precise mechanical properties which are desirable will vary with the intended use of the substrates but in general an imperfect surface e.g. one of uneven thickness or a pitted surface will not possess adequate resistance e.g. to corrosion.

The thickness of the resin coating which is deposited will be regulated according to the proposed use of the substrate. Coatings of from 1 to 20 microns e.g. 5 to 10 microns may conveniently be applied, thicker coating being applied where greater corrosion resistance is required.

The resin film is applied by making the substrate anodic in a resin bath. The rate at which the resin is deposited corresponds to the current density which is passing and hence for a particular bath and substrate is proportional to the voltage which is applied. At a constant voltage the current passing falls as the thickness of the deposited film increases until at some point deposition ceases. We prefer to employ an initial current density of from 3 to 5 amps per square foot which typically corresponds to an initial voltage of from 20 to 30 volts. Typically the deposition of the resin will be completed within a period of about 2 minutes. The application of higher initial voltages and hence the passage of higher current densities may be disadvantageous in that the deposited film may not be clear and in particular that it may lead to the deposition of gas containing resin films. If this problem is encountered a lower initial current density should be employed. Where a relatively thick deposit of resin is desired the current density can be maintained by increasing the applied voltage during the deposition as necessary. We prefer not to apply voltages of greater than 50 volts in order to minimise the likelihood of those disadvantages occurring. If the voltage applied is relatively small the rate of deposition may be reduced to an unacceptable level.

Since the quality of the film is affected by the conditions under which it is deposited any assessment of the suitability of a particular resin for use according to the present invention must be related to the conditions employed for its deposition. If the faults in the film are not too serious it may be that adjustment of the conditions under which the deposition is effected e.g. a variation in the voltage applied may produce a satisfactory product and render that particular resin useful according to the present invention.

The resin bath is typically acidic in character and is neutralised with an amine such as triethylamine and is supplied as a solution of the salt in a water miscible organic solvent. Typical solvents include the lower alcohols e.g. butanol propanol and ethanol and alkyl ether alcohols e.g. butoxyethanol.

The resin bath is conveniently formed by adding an appropriate quantity of such a resin solution to deionised water to form a suspension. The bath will preferably comprise 5 to 10% by weight of solids. Too small a concentration of resin will reduce the rate of deposition to an unacceptable level, whilst too high a concentration will increase the viscosity of the bath to unacceptable levels. The resin baths preferably comprises a water miscible organic solvent which is preferably the solvent in which the resin is dissolved. The bath will preferably comprise from 1 to 10% by weight of such a solvent, which may conveniently be provided by adding the resin to the bath as a solution in such a solvent.

The bath may also contain other conventional additives such as flow control additives, e.g. decanol. The composition of the bath is preferably monitored during its use and adjusted if necessary. For example the pH should be maintained at a value appropriate to the particular resin and the concentration of solvent and solids content of the bath should be maintained within the preferred ranges. We have discovered that the addition of small quantities of a wetting agent assists the deposition of an even film of resin and the addition of such agents to the resin bath represents a preferred aspect of the invention. Any anionic or preferably nonionic wetting agents may be employed normally in minor quantities e.g. from 10 to 200 ppm by weight of the bath. Examples of suitable wetting agents include nonyl phenol ethoxylates and fatty alcohol ethoxylates.

The substrate is preferably prepared for the deposition step by cleaning and rinsing in two stages, first with water and then with an aqueous solution of a solvent, which is preferably the solvent which is present in the resin deposition bath.

The resin coating is cured in the normal way although the coated substrate may be subjected to further treatment e.g. a dyeing process as hereinafter described prior to the curing. Typically depending upon the resin system curing is effected by stoving at elevated temperatures e.g. 100 to 250°C and more usually 150 to 200°C. We do not however exclude the use of resin systems which are curable outside these temperature ranges.

The mechanical properties of the cured film may be tested using a variety of known techniques (which are commonly destructive techniques). Amongst the common techniques which are used are a hardness test using pencils of varying hardness under standard conditions in order to ascertain which hardness marks the surface; a solvent resistance test carried out by rubbing the surface with a cloth soaked in solvent under standard conditions to ascertain whether the film is solvent resistant or a brittleness test carried out by bending the substrate to a preset degree in order to ascertain whether the film cracks. As noted above the precise properties which are acceptable will vary with the intended use of the substrate. An imperfect film will normally exhibit markedly inferior properties in one or more of these tests.

The deposited film or resin is preferably rinsed free of adherent resin solution immediately after the deposition step. Again this operation is preferably carried out in two stages using firstly an aqueous solution of a water miscible solvent which is preferably the solvent which was present in the resin bath, and secondly deionised water. We discovered that this rinsing step is surprisingly advantageous in that it appears to even out the film of uncured resin and may remove minor imperfections in the resin film. The first rinsing solution preferably contains from 0.2 to 10.0% by weight of the solvent which was present in the deposition bath.

The novel processes of the invention find particular application in the formation of evenly dyed coloured resin coatings upon metallic substrates. Since the coating is clear and is deposited evenly over the surface of the substrate dyeing can be achieved using conventional dyeing techniques. Thus dyeing may be carried out by the incorporation of a suitable water soluble dye into the solution of the resin prior to its deposition onto the substrate; by dyeing the uncured deposited resin coating in an appropriate dye bath and subsequent curing the dyed resin or by dyeing the cured resin coating in a suitable dye bath. The preferred method is to dye the uncured resin with subsequent curing of the dyed resin since the latter method requires the dyeing to be carried out at elevated temperatures whilst the former requires the provision of a separate resin bath for each dye which is to be used.

Examples of suitable dyes for use in dyeing the resin coatings are those water soluble basic dyes which form coloured cations in solution. Examples of useful dyes are certain azo dyes and certain methine dyes.

The processes of the present invention are also valuable as a step in the production of a treated metal substrate wherein the substrate is electroplated, coated with resin and dye. Since all these procedures are carried out by immersing the substrate in an aqueous liquor the substrate can be mounted on a single jig and moved from one bath to another thus facilitating the operation of the production line because there is no necessity to rejig the substrate between the individual stages in the production process.

The invention is illustrated by the following examples:-

Example 1

A cast brass component was cleaned and electroplated with nickel until a surface layer of nickel of 8 microns thickness was formed. The plated component was rinsed firstly in deionised water and secondly in a 0.5% aqueous solution of 2 butoxyethanol containing 0.5 gms/litre of paint solids whose pH had been adjusted to 8.0 with triethylamine.

The component was then immersed in an aqueous liquor containing 80 gms/litre as solid of a polyester/acrylic resin (as a 67% by weight solids solution of resin in butoxyethanol). A voltage of 20 volts was applied for 30 seconds between the component as anode and a stainless steel cathode. A film of resin of approximately 4 microns thickness was deposited over the whole surface of the component.

The coated component was rinsed firstly in a 0.5%

solution of 2-butoxy ethanol containing 0.5 gms/litre of paint solids whose pH had been adjusted to 8.0 with triethylamine, and secondly in deionised water containing 200 mg/litre of an ethoxylated nonyl phenol surfactant.

The rinsed, coated component was immersed in an aqueous dye solution (Deionised water containing 1 gm/litre of SANDOCRYL GOLDEN YELLOW B-RLN DYE, 9mls/litre of glacial acid, 1gm/litre of sodium acetate to which was added 5%v/v of 2 butoxyethanol) maintained at a temperature of 25°C for a period of 1 minute.

The dyed coated component was rinsed with water and then with a 1% v/v aqueous solution of 2 butoxyethanol adjusted to pH 8 with triethylamine.

The clean component was then stoved at 160°C for 20 minutes which completely cured the resin. A dyed coating of excellent clarity was achieved, showing no colour variation across the component which had the appearance of a lacquered brass plated component.

Example 2 Three identical substrates whose surfaces were of freshly plated bright nickel; freshly plated bright cyanide zinc and cleaned brass respectively were treated and coated with the lacquer used in Example 1 according to the procedure set out in Example 1. The substrates were stoved and their appearance compared with the following results:-

The nickel plated substrate had a clear fault free film of approximately 5 microns thickness evenly deposited on the surface thereof.

The zinc plated substrate showed some blackening in patches.

The brass substrate was coated to only 1 to 2 microns thickness, showed some attack on the surface of the substrate and some cloudiness in the film.

CLAIMS

1. A process for the production of a clear film of an anaphoretic resin upon the surface of a metallic substrate by electrodeposition which is characterised in that the surface is formed from nickel, stainless steel or aluminium and the resin is a clear resin.

2. A process according to claim 1 characterised in that the surface is formed from nickel or stainless steel.

3. A process according to either of the preceding claims characterised in that the substrate is formed from a metal other than nickel, stainless steel or aluminium onto the surface of which a layer of nickel, stainless steel or aluminium has been deposited.

4. A process according to claim 3 characterised in that the surface layer has a thickness of at least 2 microns.

5. A process according to any of the preceding claims characterised in that the resin is selected from the group comprising acrylic resins, polyester resins and modified alkyd resins, epoxy resins and combinations of these resins.

6. A process according to claim 5 characterised in that the resin is an acrylic or an acrylic/modified polyester resin.

7. A process according to any of the preceding claims characterised in that the deposition is carried out by making the substrate anodic in a resin bath.

8. A process according to claim 7 characterised in that the resin bath comprises a minor proportion of a water miscible organic solvent.

9. A process according to claim 8 characterised in that the solvent is butoxyethanol.

10. A process according to any of claims 7 to 9 characterised in that the resin bath contains a nonionic wetting agent.

11. A process according to any of claims 7 to 10 characterised in that the voltage applied across the resin bath is below that at which the deposited resin film produced contains any significant amount of trapped gases.

12. A process according to claim 11 characterised in that a voltage of from 20 to 30 volts is applied across the resin bath.

13. A process according to any of the preceding claims characterised in that the deposited film is rinsed immediately after the deposition step.

14. A process according to claim 13 characterised in that the film is rinsed firstly with an aqueous solution of a water miscible solvent and secondly with deionised water.

15. A process according to claim 14 characterised in that the solvent used in the rinse step is that which was present in the resin bath.

16. A process according to any of the preceding claims characterised in that the coated substrate is subsequently dyed using a basic dye.

17. A process according to claim 16 characterised in that the coated substrate is dyed by immersing it in a dyebath before the resin is cured.

18. A process according to any of the preceding claims substantially as herein before described with reference to the foregoing examples.

19. A coated substrate wherever produced by a process according to any of the preceding claims.

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